

WHAT IS CLAIMED IS:

1. A process for mechanosynthesizing a metal oxide having a perovskite or perovskite-like crystal structure and a predetermined stoichiometric content of oxygen, said metal oxide being selected from the group consisting of perovskites of the general formula ABO_3 ; perovskite-like materials of the general formula $[(ABO_3)_n + C_yO_z]$; non-stoichiometric compounds derived from perovskites and having the general formula (ABO_{3-x}) ; and non-stoichiometric compounds derived from perovskite-like materials and having the general formula $[(ABO_{3-x})_n + C_yO_z]$, wherein:

- A comprises at least one element selected from the group consisting of Al, Y, Na, K, Rb, Cs, Pb, La, Sr, Ba, Cr, Ag, Ca, Pr, Nd, Bi and the elements of the lanthanide series of the periodic table;
- B comprises at least one element selected from the group consisting of Al, Ga, In, Zr, Nb, Sn, Ru, Rh, Pd, Re, Os, Ir, Pt, U, Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo and W;
- C represents at least one element selected from the group consisting of Al, Ga, In, Zr, Nb, Sn, Ru, Rh, Pd, Re, Os, Ir, Pt, U, Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo, W, Al, Y, Na, K, Rb, Cs, Pb, La, Sr, Ba, Cr, Ag, Ca, Pr, Nd, Bi and the elements of the lanthanide series of the periodic table;
- n represents an integer number between 1 and 10;
- $0 < x < 3$
- y represents an integer number between 1 and 5;
- z represents an integer number between 1 and 5;

said process comprising the step of subjecting a mixture of starting powders formulated to contain the components represented by A, B and C in the formulas to a high energy milling sufficient to induce chemical reaction of the components and thereby directly mechanosynthesize said metal oxide in the form of a perovskite or a perovskite-like material having a nanocrystalline structure as determined by X-ray diffractometry.

2. The process of claim 1, characterized in that the high energy milling is performed under a controlled atmosphere to control the nanocrystalline structure and the stoichiometric oxygen content of the mechanosynthesized metal oxide.

5 3. The process of claim 2, characterized in that the atmosphere comprises a gas selected from the group consisting of He, Ar, N₂, O₂, H₂, CO, CO₂, NO₂, NH₃, H₂S and mixtures thereof.

10 4. The process of any one of claims 1 to 3, characterized in that it further comprises the step of selecting and milling the starting powders in relative portions to control the nanocrystalline structure of the mechanosynthesized metal oxide.

15 5. A process for mechanosynthesizing a metal oxide having a perovskite or perovskite-like crystal structure, and a predetermined stoichiometric content of oxygen, and a high BET specific surface area, said metal oxide being selected from the group consisting of perovskites of the general formula ABO₃; perovskite-like materials of the general formula [(ABO₃)_n + C_yO_z]; non-stoichiometric compounds derived from perovskite and having the general formula (ABO_{3-x}); and non-stoichiometric compounds derived from perovskite-like materials and having the
20 general formula [(ABO_{3-x})_n + C_yO_z], wherein:

- A comprises at least one element selected from the group consisting of Al, Y, Na, K, Rb, Cs, Pb, La, Sr, Ba, Cr, Ag, Ca, Pr, Nd, Bi and the elements of the lanthanide series of the periodic table;
- B comprises at least one element selected from the group consisting of Al, Ga, In, Zr, Nb, Sn, Ru, Rh, Pd, Re, Os, Ir, Pt, U, Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo and W;
- C represents at least one element selected from the group consisting of Ga, In, Zr, Nb, Sn, Ru, Rh, Pd, Re, Os, Ir, Pt, U, Co, Fe, Ni, Mn, Cr, Ti, Cu, Mg, V, Nb, Ta, Mo, W, Al, Y, Na, K, Rb, Cs, Pb, La, Sr, Ba, Cr, Ag, Ca, Pr, Nd, Bi and the
30 elements of the lanthanide series of the periodic table;
- n represents an integer number between 1 and 10;
- 0 < x < 3

- y represents an integer number between 1 and 5;
- z represents an integer number between 1 and 5;

said process comprising the steps of:

5 a) subjecting a mixture of starting powders formulated to contain the components represented by A, B and C in the formulas to a high energy milling sufficient to induce chemical reaction of the components and thereby directly mechanosynthesize said metal oxide in the form of a perovskite or a perovskite-like material having a nanocrystalline structure as determined by X-ray diffractometry;

10 b) increasing the BET specific surface area of the metal oxide obtained in step a) by further subjecting said metal oxide to high energy milling to obtain a metal oxide having a high BET specific surface area.

15 6. The process of claim 5, characterized in that the high energy milling of step a) is performed under a controlled atmosphere to control the nanocrystalline structure and the stoichiometric oxygen content of the mechanosynthesized metal oxide.

20 7. The process of claim 5 or 6, characterized in that that it further comprises the step of adding a small amount of an aqueous solution to the metal oxide during the milling of step b) in order to obtain a humidified metal oxide.

25 8. The process of claims 5, 6 or 7, characterized in that the high energy milling of step b) is performed under a controlled atmosphere to control the BET specific surface area of the mechanosynthesized metal oxide.

9. The process of any one of claims 5 to 8, characterized in that the atmosphere comprises a gas selected from the group consisting of H₂O, He, Ar, N₂, O₂, H₂, CO, CO₂, NO₂, NH₃, H₂S and mixtures thereof.

30 10. The process of any one of claims 5 to 9, characterized in that it further comprises the step of selecting and milling the starting powders in relative portions to control the final nanocrystalline structure of the mechanosynthesized metal oxide.

11. The process of any one of claims 5 to 10, characterized in that it further comprises the steps of:

- c) adding a non-reacting soluble additive during the milling of step b); and
5 d) subsequently washing out said soluble additive.

12. The process of claim 11, characterized in that the non-reacting soluble additive is selected from the group consisting of LiCl, NaCl, RbCl, CsCl, NH₄Cl, ZnO, NaNO₃, and mixtures thereof.

10 13. A metal oxide having a perovskite or a perovskite-like nanocrystalline structure obtained according to any one of the process of claims 1 to 12.

14. The metal oxide of claim 13 characterized in that it consists of a brownmillerite
15 having the formula $ABO_{2.5}$ or $[(ABO_{2.5})_n + C_yO_z]$.

15. The metal oxide of claim 14 characterized in that the brownmillerite is selected from the group consisting of Sr₇Fe₁₀O₂₂, SrFeO_{2.5} and SrFe_{0.5}Co_{0.5}O_{2.5}.

20 16. The metal oxide of claim 13 characterized in that it has a BET specific surface area between 3.1 and 82.5 m²/g.

17. A perovskite having the formula LaCoO₃ characterized in that it has a BET specific surface area of at least 20 m²/g.

25 18. The perovskite according to claim 17 characterized in that it has a BET specific surface area between 20 m²/g and 82.5 m²/g.

19. A perovskite having the formula CeCuO₃ characterized in that it has a BET
30 specific surface area of at least 30.3 m²/g.

20. The perovskite according to claim 19 characterized in that it has a BET specific surface area between 30.3 and 39.2 m²/g.

21. A perovskite having the formula YCoO₃ characterized in that it has a BET specific surface area of at least 9.6 m²/g.

22. The perovskite according to claim 21 characterized in that it has a BET specific surface area between 9.6 and 24.2 m²/g.

23. A perovskite having the formula La_{0.6}Sr_{0.4}CoO₃ characterized in that it has a BET specific surface area of at least 12.7 m²/g.

24. The perovskite according to claim 23 characterized in that it has a BET specific surface area between 12.7 and 30.2 m²/g.

25. A perovskite having the formula La_{0.6}Sr_{0.4}MnO₃ characterized in that it has a BET specific surface area of at least 45.4 m²/g.

26. A perovskite having the formula La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ characterized in that it has a BET specific surface area of at least 20.2 m²/g.

27. The perovskite according to claim 23 characterized in that it has a BET specific surface area between 20.2 and 47.8 m²/g.

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